



Standard Practice for Use of Statistics in the Evaluation of Spectrometric Data¹

This standard is issued under the fixed designation E 876; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{€1} NOTE—Section 7 was added editorially in January 1995.

1. Scope

1.1 This practice provides for the statistical evaluation of data obtained from spectrometrical methods of analysis. Included are definitions used in statistics, methods to determine variance and standard deviation of data, and calculations for (1) estimate of variance and pooling estimates of variance, (2) standard deviation and relative standard deviation, (3) testing for outliers, (4) testing for bias, (5) establishing limits of detection, and (6) testing for drift.

2. Referenced Documents

2.1 ASTM Standards:

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods³

E 178 Practice for Dealing with Outlying Observations³

E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves²

E 456 Terminology Relating to Quality and Statistics³

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this practice, refer to Terminologies E 135 and E 456.

3.1.2 All quantities computed from limited data are defined as estimates of the parameters that are properties of the system (population) from which the data were obtained.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *average measurement* ($\bar{x}$)—the arithmetic mean obtained by dividing the sum of the measurements by the number of measurements. It is an estimate of μ , the value of the population that the average would become if the number of measurements were infinite. Either $\bar{x}$ or μ may include a systematic error if there is a bias in the measurement.

3.2.2 *bias*—a systematic displacement of all or most deter-

minations from the assumed true value. An acceptable bias should be agreed upon prior to testing a method. *Accuracy*, often used to qualify a method, is a measurement which includes both imprecision and bias.

NOTE 1—*Precision* and *bias* are discussed in detail in Practice E 177. In analytical methods, *precision* refers to the distribution of repeat determinations about the average. All analyses are presumed to have been made under the same set of conditions. Standard deviation provides a measure of this distribution.

NOTE 2—An evaluation of a method will be sample-dependent. Multiple samples should be tested for homogeneity since even certified reference materials may exhibit significantly different degrees of inhomogeneity. A measure of both sample and method precision may be made by replicating determinations on specific portions of the sample specimens.

3.2.3 *confidence to be placed on the estimate of μ* (μ)—the average, $\bar{x}$, is expected to be close to μ and should be very close if the number of determinations is large, no significant bias exists and the standard deviation, s , is small. The degree of closeness is expressed as a probability (*confidence level*) that μ is in a specified interval (*confidence interval*) centered at $\bar{x}$. With a certain probability, limits are placed on the quantity $\bar{x}$ which may include the unknown quantity μ . A probability level, p %, can be selected so that μ will be within the limits placed about $\bar{x}$. See 3.2.1

3.2.4 *degrees of freedom (df)*—the number of contributors to the deviations of a measurement. Since a deviation can be implied only when there are at least two members of a group, the degrees of freedom of a set of measurements is generally one less than the number of measurements. It is the sample size less the number of parameters estimated. If the group is a listing of a series of differences of measurements or a series of determinations of variance, the degrees of freedom is the number of these differences or the total of the degrees of freedom of each series of determinations.

3.2.5 *detection limit*—paraphrasing the definition in Terminology E 135, it is the lowest estimated concentration that permits a confident decision that an element is present. The actual concentration being measured falls within a confidence interval that encompasses the estimated concentration. The lowest estimate has a confidence interval that reaches to zero concentration, but not below. It cannot be assumed that the estimated concentration is an actual concentration. Neither can it be assumed that an actual concentration that equals the

¹ This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.

Current edition approved Nov. 20, 1989. Published January 1990. Originally published as E 876 – 82. Last previous edition E 876 – 89.

² Annual Book of ASTM Standards, Vol 03.05.

³ Annual Book of ASTM Standards, Vol 14.02.